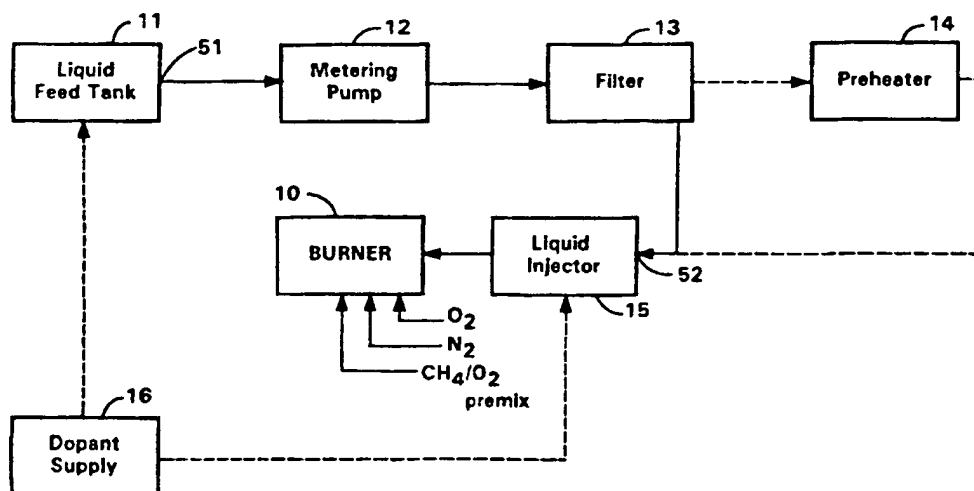




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C01B 33/12, B05B 1/28		A1	(11) International Publication Number: WO 97/22553
			(43) International Publication Date: 26 June 1997 (26.06.97)
(21) International Application Number: PCT/US96/20756		(81) Designated States: AU, BR, CA, CN, JP, KR, MX, RU, UA, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(22) International Filing Date: 12 December 1996 (12.12.96)			
(30) Priority Data: 60/008,889 19 December 1995 (19.12.95) US		Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(71) Applicant (for all designated States except US): CORNING INCORPORATED [US/US]; 1 Riverfront Plaza, Corning, NY 14831 (US).			
(72) Inventors; and			
(75) Inventors/Applicants (for US only): HAWTOF, Daniel, W. [US/US]; 40 Fox Lane Extension, Painted Post, NY 14870 (US). HENDERSON, Danny, L. [US/US]; 306 Brookshire Lane, Wilmington, NC 28408 (US). SMITH, Greg, E. [US/US]; 10847 Hidden Meadow Trail, Corning, NY 14830 (US). URRUTTI, Eric, H. [US/US]; 43 Orchard Drive, Big Flats, NY 14814 (US).			
(74) Agent: HERZFELD, Alexander, R.; Corning Incorporated, Patent Dept., SP FR 02-12, Corning, NY 14831 (US).			

(54) Title: METHOD AND APPARATUS FOR FORMING FUSED SILICA BY COMBUSTION OF LIQUID REACTANTS



(57) Abstract

The present invention is directed to a method for making fused silica glass by introducing a liquid, preferably halide-free, silicon-containing compound (32) directly into the flame (23) of a burner (24), thereby forming amorphous soot (25). This soot is deposited on a surface (26) and consolidated into a body of fused silica glass. The invention also relates to an apparatus which includes a burner (24) which generates a flame (23); an injector (31) for supplying a compound (32) to the flame (23) to convert the compound to soot and a surface (26) on which the soot is deposited.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

METHOD AND APPARATUS FOR FORMING FUSED SILICA
BY COMBUSTION OF LIQUID REACTANTS

5

FIELD OF THE INVENTION

The present invention relates to the formation of
fused silica and, more particularly, to a method and
10 apparatus for forming fused silica from liquid silicon-
containing compounds.

BACKGROUND OF THE INVENTION

15 Various processes are known in the art that involve
the production of metal oxides from vaporous reactants.
Such processes require a feedstock solution, a means of
generating and transporting vapors of the feedstock
solution (hereafter called vaporous reactants) and an
20 oxidant to a conversion reaction site, and a means of
catalyzing oxidation and combustion coincidentally to
produce finely divided, spherical aggregates, called soot.
This soot can be collected on any deposition receptor in
any number of ways ranging from a collection chamber to a
25 rotating mandrel. It may be simultaneously or
subsequently heat treated to form a non-porous,
transparent, high purity glass article. This process is

-2-

usually carried out with specialized equipment having a unique arrangement of nozzles and burners.

5 Much of the initial research that led to the development of such processes focused on the production of bulk fused silica. Selection of the appropriate feedstock was an important aspect of that work. Consequently, it was at that time determined that a material capable of generating a vapor pressure of 200-300 millimeters of mercury (mm Hg) at temperatures below 100°C would be
10 useful for making such bulk fused silica. The high vapor pressure of silicon tetrachloride (SiCl_4) suggested its usefulness as a convenient vapor source for soot generation and launched the discovery and use of a series of similar chloride-based feedstocks. This factor, more
15 than any other, is responsible for the presently accepted use of SiCl_4 , GeCl_4 , POCl_3 , and BCl_3 as vapor sources, even though these materials have certain chemically undesirable properties.

Silicon, germanium, zirconium, and titanium are
20 metals often used in halide form as vaporous reactants in forming metal oxide glasses. However, SiCl_4 has been the industry standard over the years for the production of high purity silica glasses. As disclosed in U.S. Patent No. 3,698,936, one of several reactions may be employed to
25 produce high purity fused silica via oxidation of SiCl_4 ; namely:

- (1) $\text{SiCl}_4 + \text{O}_2 \rightarrow \text{SiO}_2 + 2\text{Cl}_2$,
- (2) $\text{SiCl}_4 + \frac{2}{3}\text{O}_3 \rightarrow \text{SiO}_2 + 2\text{Cl}_2$, or
- 30 (3) $\text{SiCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{HCl}$,

whereby burners or jet assemblies are utilized in feeding the reactant gases and vapors to a reaction space. It should be noted that reaction (2) rarely occurs or is
35 used. There are inherent economic disadvantages to each

-3-

of these reactions. Moreover, these reactions, which oxidize SiCl_4 through pyrolysis and hydrolysis, have the disadvantage of producing chlorine or a very strong acid by-product.

5 While the first two reactions occur theoretically, an auxiliary fuel is generally needed to achieve pyrolytic temperature. The hydrolysis of SiCl_4 results in the formation of hydrochloric acid (HCl), a by-product that is detrimental not only to many deposition substrates and to
10 reaction equipment but also is harmful to the environment. Emission abatement systems have proven to be very expensive due to down-time, loss, and maintenance of equipment caused by the corrosiveness of HCl .

 Notwithstanding the problems with handling and
15 disposal of the HCl by-product, the third reaction, hydrolysis of SiCl_4 , tends to be the preferred commercial method of producing fused silica for economic reasons.

 Though hydrolysis of SiCl_4 has been the preference of industry for producing high purity fused silica over the
20 years, the enhanced global sensitivity to environmental protection has led to more strict government regulation of point source emissions, prompting a search for less environmentally pernicious feedstocks. Point source emission regulations require that HCl , the by-product of
25 hydrolyzing SiCl_4 , as well as many particulate pollutants be cleansed from exhaust gases prior to their release into the atmosphere. The economic consequences of meeting these regulations have made commercial production of fused silica from halide-based feedstocks less attractive to
30 industry.

 As an alternative, high purity fused quartz or silica has also been produced by thermal decomposition and oxidation of silanes. However, this requires taking
35 safety measures in handling because of the violent reaction that results from the introduction of air into a

-4-

closed container of silanes. Silanes react with carbon dioxide, nitrous oxide, oxygen, or water to produce high purity materials that are potentially useful in producing, among other things, semiconductor devices. However, silanes have proven to be much too expensive and reactive to be considered for commercial use except possibly for small scale applications requiring extremely high purity.

A number of patents describe the production of high purity metal oxides, particularly fused silica, from a chloride-based feedstock. These patents disclose equipment with a number of burner arrangements and feedstock delivery systems to achieve oxidation of a metal chloride through flame hydrolysis or pyrolysis. Illustrative of this is U.S. Patent No. 4,491,604 to Lesk et al., where trichlorosilane, dichlorosilane, and silicon tetrachloride are flame hydrolyzed to form soot, and U.S. Patent No. 3,666,414 to Bayer, where silicon halides such as trichlorosilane or chloroform are flame hydrolyzed. In similar processes, U.S. Patent Nos. 3,486,913 to Zirngibl ("Zirngibl") and 2,269,059 to McLachlan ("McLachlan") teach oxidation of halides. Volatilized inorganic halide components such as TiCl_4 , CrCl_3 , CrO_2Cl_2 , SiCl_4 , AlCl_3 , ZrCl_4 , FeCl_2 , FeCl_3 , ZnCl_2 , or SnCl_4 that are oxidized with air, steam, or oxygen are employed in Zirngibl, while silicon halides, ethyl silicate, methyl borate, TiCl_4 , AlCl_3 , and ZrCl_4 are used by McLachlan.

U.S. Patent No. 3,416,890 to Best et al. discloses a process for preparing finely-divided metal or metalloid oxides by the decomposition of a metal or metalloid perhalide in a flame produced by the combustion of an oxidizing gas and an auxiliary fuel, such as carbon disulfide, carbon selenide sulfide, thiophosgene, or other hydrogen-free compounds containing sulfur bonded directly to carbon.

U.S. Patent No. 2,239,551 to Dalton discloses a method of making glass by decomposing a gaseous mixture of glass-forming compounds in a flame of combustible gas. The mixture is used in the formation of anhydrous oxides of silicon, aluminum, and boron. Decomposable compounds such as ethyl or methyl silicate, trichlorosilane, and silicon tetrafluoride may be substituted for silicon tetrachloride; methyl borate or boron hydride may be substituted for boron fluoride, etc.

U.S. Patent No. 2,326,059 to Nordberg details a technique for making silica-rich ultra-low expansion glass by vaporizing tetrachlorides of Si and Ti into the gas stream of an oxy-gas burner, depositing the resultant mixture to make a preform, vitrifying the preform at 1500°C to make an opal glass, and firing the opal preform at a higher temperature to cause it to become transparent.

U.S. Patent No. 2,272,342 to Hyde discloses a method of producing glass articles containing vitreous silica by vaporizing a hydrolyzable compound of silicon such as silicon chloride, trichlorosilane, methyl silicate, ethyl silicate, silicon fluoride, or mixtures thereof, using a water bath. The silicon compound vapor is hydrolyzed by water vapor in the flame of a burner, and the resulting amorphous oxide is collected and subsequently sintered until a transparent glass results.

U.S. Patent No. 4,501,602 to Miller et al. describes the production of particulate metal oxide soot through the vapor phase deposition of β -diketonate complexes of metals from Groups IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, and the rare earth series of the Periodic Table.

Also cited in the art are several patents where silane compounds have been used in producing high purity fused silica.

Japanese Patent Application No. 90838-1985 to Okamoto et al., discloses a method of doping quartz glass by

-6-

utilizing an ester silane expressed by the general formula $R^1_nSi(OR^2)_{4-n}$ and one or more dopants defined by the formulae $Ge(OR^3)_3$, $B(OR^3)_3$, and PH_3 , where R^1 is a hydrogen atom, methyl or ethyl group; R^2 is a methyl or ethyl group; R^3 is an univalent hydrocarbon group; and n is an integer ranging between 0 and 4. A great many organometallic compounds are disclosed, including methyltrimethoxysilane, dimethyldimethoxysilane, trimethylmethoxysilane, tetramethoxysilane, methyltriethoxysilane, and tetraethoxysilane.

U.S. Patent No. 3,117,838 to Sterling describes a method of producing very pure fused quartz or silica by the combined thermal decomposition and oxidation of silanes where either carbon dioxide, nitrous oxide, or water vapor and a silane are fed into a burner or torch jet, and the flame is allowed to impinge on a carbon substrate upon which silica is deposited.

U.S. Patent No. 4,810,673 to Freeman discloses a method of synthesizing high quality silicon oxides by chemical vapor deposition of a source gas mixture which includes a halogenated silane component and an oxygen source, namely, dichlorosilane and nitrous oxide.

U.S. Patent No. 4,242,487 to Hasegawa et al. discloses a method of producing a heat resistant, semi-inorganic compound that is useful as a material for various heat-resistant materials by reacting an organoborosiloxane compound with at least one of the group of aliphatic polyhydric alcohols, aromatic alcohols, phenols, and aromatic carboxylic acids at 250°C to 450°C in an inert atmosphere.

As is clear from the preceding discussion, it is highly desirable for both economic and environmental reasons to find halide-free silicon compounds to replace the silicon halide feedstocks typically used to produce high purity silica glass. Such halide-free starting

-7-

materials would produce carbon dioxide and water, rather than noxious and corrosive HCl, as by-products of the glass-making process.

U.S. Patent No. 5,043,002 to Dobbins et al., the disclosure of which is hereby incorporated by reference, discloses the usefulness of polymethylsiloxanes, in particular, polymethylcyclotrisiloxanes such as hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane ("OMCTS"), and decamethylcyclopentasiloxane in a method of making fused silica glass. The method can be applied to the production of a non-porous body of silica glass doped with various oxide dopants and for the formation of optical waveguide fibers. U.S. Patent No. 5,043,002 to Dobbins et al. also discloses the use of hexamethyldisiloxane; see also reference to hexamethyldisiloxane in Japanese Patent Application No. 1-138145.

U.S. Patent No. 5,152,819 to Blackwell et al., the disclosure of which is hereby incorporated by reference, describes additional halide-free silicon compounds, in particular, organosilicon-nitrogen compounds having a basic Si-N-Si structure, siloxasilazones having a basic Si-N-Si-O-Si structure, and mixtures thereof, which may be used to produce high purity fused silica glass without the concomitant generation of corrosive, polluting by-products.

Although use of halide-free silicon compounds as feedstocks for fused silica glass production, as described in U.S. Patent Nos. 5,043,002 and 5,152,819, avoids the formation of HCl, some problems remain, particularly when the glass is intended for the formation of optical waveguide fibers. Applicants have found that, in the course of delivering a vaporized polyalkylsiloxane feedstock to the burner, high molecular weight species can be deposited as a gel in the line carrying the vaporous

-8-

reactants to the burner or within the burner itself. This leads to a reduction in the deposition rate of the soot preform that is subsequently consolidated to a blank from which an optical waveguide fiber is drawn. It also leads to imperfections in the blank that will produce defective or unusable optical waveguide fiber from the affected portions of the blank.

SUMMARY OF THE INVENTION

The present invention is directed to a method for making fused silica glass. A liquid, preferably halide-free, silicon-containing compound capable of being converted by thermal oxidative decomposition to SiO_2 is provided and introduced directly into the flame of a combustion burner, thereby forming finely divided amorphous soot. The amorphous soot is deposited on a receptor surface where, either substantially simultaneously with or subsequently to its deposition, the soot can be consolidated into a body of fused silica glass. The body of fused silica glass can then be either used to make products directly from the fused body, or the fused body can be further treated, e.g., by drawing to make optical waveguide fiber further see, e.g., the end-uses described in the U.S. Patent Application No. 08/574,961 entitled "Method for Purifying Polyalkylsiloxanes and the Resulting Products", the contents of which are hereby incorporated by reference.

The invention further comprises an apparatus for forming fused silica from liquid, preferably halide-free, silicon-containing reactants that comprises: a combustion burner which, in operation, generates a conversion site flame; an injector for supplying a liquid silicon-containing compound to the flame to convert the compound

by thermal oxidative decomposition to a finely divided amorphous soot; and a receptor surface positioned with respect to said combustion burner to permit deposition of the soot on the receptor surface.

5 Forming amorphous fused SiO_2 soot particles from a feedstock comprising a volatile silicon-containing compound typically entails vaporization of that compound prior to its introduction into a combustion burner. In the previously mentioned U.S. Patent No. 5,043,002 to
10 Dobbins et al., for example, a carrier gas such as nitrogen is bubbled through a silicon-containing reactant compound, preferably a halide-free compound such as octamethylcyclotetrasiloxane. A mixture of the reactant compound vapor and nitrogen is transported to the burner
15 at the reaction site, where the reactant is combined with a gaseous fuel/oxygen mixture and combusted.

 Although use of halide-free silicon compounds as feedstocks for fused silica glass production, as described in U.S. Patents Nos. 5,043,002 and 5,152,819, avoids the
20 formation of HCl , some problems remain, particularly when the glass is intended for the formation of high quality optical products such as optical waveguide fibers. Applicants have found, as disclosed in copending U.S. Patent Application No. 08/574,961 entitled "Method for
25 Purifying Polyalkylsiloxanes and the Resulting Products", that the presence of high boiling point impurities in, for example, a polyalkylsiloxane feedstock, can result in the formation of gel deposits in the vaporization and delivery systems carrying the vaporous reactants to the burner or
30 within the burner itself. Such polymerizing and gelling of the siloxane feedstock inhibits the controllability and consistency of the silica manufacturing process. This problem is aggravated when an oxidizing carrier gas such as oxygen is included in the reactant vapor stream,
35 because oxidizers can catalyze polymerization of the

-10-

siloxane feedstock. This leads to a reduction in the deposition rate of the soot preform that is subsequently consolidated to a blank from which an optical waveguide fiber is drawn. Furthermore, particulates of the high molecular weight, high boiling impurities may be deposited on the optical waveguide fiber blank, resulting in "defect" or "clustered defect" imperfections that adversely affect the quality of the subsequently drawn optical waveguide fiber and can require scrapping of an entire blank.

Defects are small (i.e. 0.1 to 4.0 mm in diameter) bubbles in a glass body. They can be formed in fused silica by an impurity, such as uncombusted gelled polyalkylsiloxane. A very small particle of siloxane gel can be the initiation site for a defect. The siloxane decomposes at high temperature after being deposited on the glass body, giving off gases which cause the formation of the defect.

Thermophoresis is the process by which soot is attracted to the preform. In fact, it produces the driving force which moves the particles towards the cooler preform. The hot gases from the burner pass around the preform during laydown; the soot particles do not have sufficient momentum by combustion alone to strike the preform. Thermophoresis moves particles in a temperature gradient from hot regions to cooler regions. The burnt gases from a burner are hotter than the preform. As these gases pass around the preform, a temperature gradient is produced. Hot gas molecules have higher velocity than cold gas molecules. When hot gas molecules strike a particle, they transmit more momentum to the particle than a cold gas molecule does. Thus, particles are driven towards the colder gas molecules and, in turn, toward the preform.

-11-

Clustered defects are larger glass defects found in optical waveguide fiber preforms. They are made up of a series of defects in the form of a line or a funnel- or flower-shaped cluster. A large particle of gel can be the initiation site for a clustered defect. After the gel particle has struck the porous preform, it causes a raised area to stand out from the preform surface. Because the clustered defect is a raised site, more heat transfer passes to this site. Because of this increased heat transfer, more thermophoresis occurs at this site, causing the imperfection to grow and leave behind a string of defects. As a result of the clustered defect, the affected portion of the optical waveguide fiber preform cannot be consolidated normally, and the consequent irregularity in the blank yields defective optical waveguide fiber. In the case of a typical 100 kilometer consolidated blank, which has a diameter of 70 millimeters (mm) and a length of 0.8 meter (m), the presence of one clustered defect on the surface of the blank will typically result in the loss of 5 kilometers of optical waveguide fiber on drawing. In the case of a larger consolidated blank, the negative impact of a single clustered defect is proportionately higher. In a 250 kilometer consolidated blank, which has a diameter of 90 mm and a length of 1.8 m, one clustered defect on the surface of the blank will typically result in the loss of 8 kilometers of optical waveguide fiber on drawing.

The applicants have now discovered that the above-described problem is inhibited by delivering the siloxane feedstock in the liquid form to the conversion site during the silica manufacturing process. By delivering the siloxane feedstock as a liquid instead of as a vapor, gelling of the siloxane feedstock is prevented in that exposure of the siloxane feedstock to the high temperature environments of a vaporizer and vapor delivery system are

-12-

avoided. This improves the yield and quality of the fused silica produced and also reduces the maintenance requirements of the production system.

5

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a block diagram of a reactant delivery system in accordance with the present invention.

10

FIG. 2 is a schematic representation of liquid reactant provided to the flame of a burner from a syringe in accordance with the present invention.

15

FIG. 3 is a schematic representation of liquid reactant particles being provided to the flame of a burner from a transducer in accordance with the present invention.

20

FIG. 4 is a schematic representation of an atomizer incorporated into the structure of a burner in accordance with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

25

The present invention is directed to a method for making a high purity fused silica glass. The invention provides a method of inhibiting the gelling of a siloxane feedstock in the silica manufacturing process by delivering the siloxane feedstock to the conversion site in a liquid form. Since the hot environments of the vaporizer and vapor delivery system, which promote the formation of troublesome gels, are avoided, the silica manufacturing process is improved. The siloxane feedstock is delivered to the conversion site as a liquid and does not vaporize until just prior to or simultaneous with

30

35

-13-

being converted into amorphous silica soot. The amorphous silica soot is then deposited on a receptor surface.

Either substantially simultaneously with or subsequently to its deposition, the soot can be consolidated into a body of fused silica glass, from which e.g., an optical waveguide fiber can be formed by drawing.

The invention further comprises a silica manufacturing apparatus which includes a siloxane liquid feedstock tank for containing the siloxane liquid feedstock and a siloxane liquid feedstock transporting conduit for delivering the siloxane liquid feedstock to an injector which injects the liquid feedstock into the conversion site where it is decomposed in a combustion burner flame to form a finely divided amorphous silica soot which is deposited on a receptor surface.

The body of fused silica glass can be doped with an oxide dopant wherein, in addition to the liquid siloxane feedstock, a dopant compound that is capable of being converted by oxidation or flame hydrolysis to a member of the group consisting of P_2O_5 and a metal oxide having a metal component selected from Groups IA, IB, IIA, IIB, IIIA, IIIB, IVA, VA, and the rare earth series of the Periodic Table of Elements is introduced into the flame of the burner. The oxide-doped fused silica glass so obtained can be, e.g., drawn into an optical waveguide fiber.

FIG. 1 schematically depicts a system for delivering liquid siloxane feedstock and, optionally, dopant-providing compounds to burner 10. A liquid siloxane feedstock such as a polymethylcyclsiloxane is stored in feedstock tank 11. Feedstock tank 11 is connected to liquid feedstock injector 15 at the reactant introduction site via a liquid feedstock transporting conduit system that can, if desired, include metering pump 12, optional filter 13, and preheater 14. Said

-14-

liquid feedstock transporting conduit has a first terminal end 51 and a second terminal end 52. The siloxane feedstock liquid from tank 11 is transferred through the liquid feedstock transporting conduit by pump 12 through filter 13 to optional preheater 14. The liquid delivered through filter 13 is under sufficient pressure to substantially prevent and inhibit its volatilization in preheater 14, which is optionally employed to warm the liquid reactant prior to its introduction into burner 10 and avoids the high temperatures of a vaporizer which normally promote gel formation. The burner preferably is conventionally provided with inner shield gas, outer shield gas, and a mixture of methane and oxygen for the flame, as described, for example, in U.S. Patent No. 4,165,223 to D.R. Powers, which is hereby incorporated by reference.

The liquid reactant is conveyed from optional filter 13 or optional preheater 14 through second terminal end 52 to liquid injector 15, which delivers the liquid to burner 10. Injector 15 comprises a device for delivering the liquid reactant, either as a liquid stream or as atomized liquid particles, directly into the flame of burner 10. We generally refer in the discussion to the reactant as being in "liquid" form. What we mean by that expression is that the reactant is in a substantially liquid state. Some small portion of the reactant may be in vapor form, particularly where preheater 14 is employed, or where a nitrogen blanket over the liquid is employed. A small portion of the reactant can be in vapor form as delivered to the combustion site without adversely affecting the operation of the invention.

Liquid injector 15 can comprise, for example, a syringe provided with a fine needle, by which a liquid stream can be injected at high velocity into the burner flame. Although a syringe can be used on a small scale,

-15-

commercial operations will require a reasonable large scale equivalent, e.g., an atomizer.

Several types of atomizing means capable of forming very small particles of liquid are known in the atomization art as disclosed in Atomization and Sprays, by Arthur H. Lefebure, Hemisphere Publishing Co., 1989, which is incorporated herein by reference. Atomizers can be operated by various energy sources such as liquid, gas, mechanical, electrical and vibrational, and may be categorized as, for example, jet, swirl, jet-swirl, pneumatic, rotary, acoustic, ultrasonic, and electrostatic. Preferably, a jet atomizer is used; even more preferably, the jet atomizer is a swirl-jet atomizer, which swirls the liquid and then, as atomizers generally do, squirts the liquid at high velocity out of a small orifice. Various types of atomizers are discussed in Liquid Atomization, by L. Bayvel and Z. Orzechowski, Taylor & Francis, (1993), which is hereby incorporated by reference.

Another preferred type is a pneumatic atomizer operated by nitrogen or air pressure. In particularly preferred embodiments, the atomizer can be incorporated into the structure of the combustion burner.

The atomized particles of the siloxane reactant compound are combusted in a burner fueled by, preferably, a combination of methane and oxygen. The atomized reactant particles can be conveyed from the atomizer to the burner flame by a carrier gas such as nitrogen, which is preferably the atomizing gas.

FIG. 2 schematically depicts an apparatus in accordance with the present invention, in which syringe 21 injects a liquid reactant stream 22 into conversion site flame 23 produced by burner 24. Thermal oxidative decomposition of the reactant produces finely divided amorphous soot 25, which is deposited on rotatable mandrel 26.

-16-

FIG. 3 is a schematic representation of another embodiment of the apparatus of the present invention, whereby atomizer 31 injects small liquid reactant particles 32 into flame 23 produced by burner 24.

5 Combustion of the reactant yields soot 25, which is deposited on rotatable mandrel 26.

FIG. 4 is a cross-sectional view of a preferred embodiment of the apparatus of the present invention. Here, burner 40 incorporates within its structure atomizer 41, which injects very finely atomized liquid reactant particles into flame 23. As with the previously described embodiments, amorphous soot 25 produced by combustion of the liquid reactant is collected on rotatable mandrel 26.

10 As shown in FIG. 4, burner 40 comprises a series of concentric channels surrounding atomizer 41. A stream of nitrogen may be delivered via innermost channel 43 to forestall premature contact of reactant particles 42 with oxygen, which may be delivered to flame 23 through channels 44 and 45. A premix of oxygen and a fuel such as methane is conducted to the flame through outermost channel 46. A burner fitted with an atomizing injector, such as the embodiment depicted in FIG. 4, produces a wide soot stream, which achieves improved concentricity of the core and cladding regions of a subsequently formed optical waveguide fiber.

15 The most preferred atomizer unit 53 of the invention as shown in FIG. 4 is comprised of an airblast atomizer. With such an airblast atomizer, the liquid siloxane feedstock is atomized by the kinetic energy of a flowing gas stream such as from inner most channel 43. High velocity gas is utilized in atomizing the feedstock. This produces atomized liquid projections 42 with a velocity in the range of 0.5 to 50.0 m/sec. The use of an inert gas is preferred with the airblast atomizer. N₂ gas is particularly preferred with the invention, but a non-inert gas such as O₂ could be used but will not help to prevent

-17-

combustion of the feedstock prior to full vaporization of the liquid feedstock. Use of N_2 gas as the airblasting gas helps to blanket the feedstock from the oxygen in the flame and prevents burner buildup. With the use of
5 airblast atomizer in the invention, the high velocity blast gas is deployed in an effective manner to achieve a beneficial level of atomization of the siloxane at the burner and in the flame.

In practicing the invention, even though it is
10 preferred to have atomizer unit 53 as an integral part of the burner unit, it is possible to use an airblast atomizer which is spatially separated from the burner, as with atomizers 21 and 31 in FIG. 2 and FIG. 3.

The apparatus can also be provided with dopant supply
15 tank 16, shown in FIG. 1, which contains a compound capable of being converted by oxidation or flame hydrolysis to P_2O_5 or to a metal oxide whose metallic component is selected from Groups IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA, and the rare earth series of the
20 Periodic Table. These oxide dopants combine with the silica generated in the burner to provide doped silica glass, which can be subsequently formed into optical waveguide fibers.

The compound that provides the silica glass dopant
25 can be provided to feed tank 11 from dopant supply 16 of FIG. 1. Alternatively, the dopant can be delivered from supply 16 to liquid injector 15 via a separate metering pump and optionally a filter (not shown) analogous to the delivery system used for the silicon-containing compound.

In accordance with the invention, the preferably
30 halide-free, silicon-containing reactant compound preferably comprises a polyalkylsiloxane, for example, hexamethyldisiloxane. More preferably, the polyalkylsiloxane comprises a polymethylcyclsiloxane.
35 Most preferably, the polymethylcyclsiloxane is selected from the group consisting of hexamethylcyclotrisiloxane,

-18-

octamethylcyclotetrasiloxane,
decamethylcyclopentasiloxane,
dodecamethylcyclohexasiloxane, and mixtures thereof.

As disclosed in copending U.S. Patent Application No.
5 08/574,961, the use of such siloxane feedstocks as
octamethylcyclotetrasiloxane poses problems with the
conventional silica manufacturing process in that the
siloxane feedstock is prone to polymerize and form gels,
which clog and impede the feedstock vaporizer and
10 vaporized feedstock delivery system.

The following examples further illustrate the
invention.

15 Example 1 - Soot Generation by Injection of Liquid
Reactant into a Flame with a Syringe

A stream of liquid octamethylcyclotetrasiloxane
(OMCTS) was injected into a burner flame of a lathe fitted
20 with a glass rod using a syringe provided with a 0.01-inch
diameter needle. The resulting porous soot particles
containing SiO_2 were collected on the rotating one-inch
diameter glass rod. This procedure demonstrates the
feasibility of obtaining SiO_2 by combustion of the siloxane
25 feedstock compound in liquid form.

Example 2 - Generation of Soot Using an Ultrasonic
Transducer Atomizer as Injector

30 Liquid octamethylcyclotetrasiloxane (OMCTS) was
delivered to a combustion burner via a Vibra-Cell® 20-khz
ultrasonic transducer atomizer (available from Sonics &
Materials, Inc., Danbury, CT) inserted down the centerline
35 of the burner. The atomizer was surrounded by two inner
rings of oxygen supply and an outer ring of premixed
 CH_4/O_2 . The following flow rates were employed:
octamethylcyclotetrasiloxane (OMCTS), 11 grams per minute;

-19-

oxygen, 10 standard liters per minute (SLPM); premix, 10 SLPM CH₄ and 8.4 SLPM O₂.

Combustion was continued for about 10 minutes. A good deposit of SiO₂ soot was collected on the mandrel, further demonstrating the practicality of producing SiO₂ from a siloxane feedstock introduced as small liquid particles into the burner flame.

Example 3 - Soot Generation by an Atomizing Combustion Burner

An atomizing burner was constructed as depicted in FIG. 4. Various dimensions of atomizer 41 and the surrounding channels were tested, as follows:

inner diameter of atomizer 41: 0.007 to 0.015 inch
inner diameter of channel 43: 0.036 to 0.050 inch
outer diameter of channel 43: 0.048 to 0.063 inch

Using an atomizer 41 having an 0.015-inch inner diameter, particles of soot were generated from octamethylcyclotetrasiloxane (OMCTS) for 65 minutes. Flow rates were as follows:

Premix through channel 46: 10 SLPM CH₄ and 8 SLPM O₂.
O₂ through channels 44 and 45: 26 SLPM.
N₂ through channel 43: 5.6 SLPM.

Octamethylcyclotetrasiloxane (OMCTS) through atomizer 41: 6 milliliters per minute (ml/min) for first five minutes, then 10 ml/min for next 60 minutes.

The target or bait, a 1-inch diameter glass rod, was set to rotate between 1 and 5 rotations per second, traversing back and forth at about 15 meters per minute.

-20-

The burner to bait receptor surface distance was about 6.5 inches.

Complete combustion of the reactant octamethylcyclotetrasiloxane (OMCTS) was achieved, and the target weight
5 increased by 247 grams over the 65-minute deposition period (3.8 grams/minute). The soot was subsequently consolidated in a furnace, yielding glass that was clear and free of visible defects.

These results demonstrate the successful use of an
10 atomizing burner of the invention to combust a liquid siloxane feedstock and deposit soot on a receptor surface at a good rate.

The invention has been described in detail for the purpose of illustration, but it is understood that such
15 detail is solely for that purpose and variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention, which is defined by the following claims.

-21-

What is claimed:

1. A method of inhibiting the gelling of a siloxane feedstock during the manufacturing of silica, said method
5 comprised of the steps of:
 - a) obtaining a liquid siloxane feedstock;
 - b) delivering said liquid siloxane feedstock in the liquid form to a conversion site;
 - c) atomizing said liquid siloxane feedstock at the
10 conversion site;
 - d) converting said atomized siloxane feedstock at the conversion site into silica.
2. A method as claimed in claim 1, wherein said step of
15 atomizing said liquid siloxane feedstock at the conversion site, further comprises the step of airblast atomizing said liquid siloxane feedstock.
3. A method as claimed in claim 2, wherein said step of
20 airblast atomizing said liquid siloxane feedstock further comprises the step of atomizing the liquid siloxane feedstock with the kinetic energy of a flowing gas stream.
4. A method as claimed in claim 2, wherein said step of
25 airblast atomizing said liquid siloxane feedstock further comprises the step of airblasting said liquid siloxane feedstock with an inert gas.
5. A method as claimed in claim 4, wherein said step of
30 airblasting said liquid siloxane feedstock with an inert gas comprises the step of airblasting said liquid siloxane feedstock with nitrogen gas.
6. A method as claimed in claim 1, wherein said step of
35 atomizing said liquid siloxane feedstock at the conversion

-22-

site, further comprises imparting a velocity of greater than 0.5m/sec to the atomized siloxane feedstock.

5 7. A method as claimed in claim 1, wherein said step of converting said atomized siloxane feedstock at the conversion site into silica, further comprises the step of decomposing said atomized siloxane feedstock in a flame.

10 8. A method of utilizing a liquid siloxane at a conversion site where the siloxane is converted into silica soot, said method comprised of the steps of:

a) containing a liquid siloxane at a location remote from said conversion site;

15 b) delivering said liquid siloxane in the liquid form to the conversion site;

c) vaporizing said delivered liquid siloxane at the conversion site;

20 d) converting said vaporized delivered siloxane into silica soot at the conversion site.

25 9. A method as claimed in claim 8, wherein said step of delivering said liquid siloxane in the liquid form to the conversion site further comprises the step of inhibiting the vaporization of the liquid siloxane.

10. A method as claimed in claim 8, wherein said step of vaporizing said delivered liquid siloxane further comprises the step of blasting said liquid siloxane with an inert gas.

30 11. A method as claimed in claim 8, said method further comprising the step of doping said silica soot with at least one member of a group consisting of P_2O_5 and a metal oxide having a metallic component selected from Groups IA,

-23-

IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA, and the rare earth series of the Periodic Table of Elements.

5

12. A silica manufacturing apparatus comprised of:

a siloxane liquid feedstock tank containing a siloxane liquid feedstock;

10

a siloxane liquid feedstock delivery conduit having a first terminal end and a second terminal end, said first terminal end connected to said siloxane liquid feedstock tank;

15

a siloxane liquid feedstock injector, said injector connected to the second terminal end of said siloxane liquid feedstock delivery conduit;

20

a siloxane to silica conversion site proximate said injector, wherein siloxane projected from said injector is converted into silica.

25

13. A silica manufacturing apparatus as claimed in claim 12, wherein said siloxane liquid feedstock injector is comprised of a means for atomizing.

30

14. An apparatus as claimed in claim 13, wherein said means for atomizing is comprised of an airblast atomizer.

15. An apparatus as claimed in claim 14, wherein said airblast atomizer is adjacent to a burner.

-24-

16. An apparatus as claimed in claim 12, wherein said siloxane to silica conversion site is comprised of a flame.

5 17. An apparatus as claimed in claim 13, wherein said means for atomizing is comprised of an electrostatic atomizer.

10 18. An apparatus as claimed in claim 13, wherein said means for atomizing is comprised of a pneumatic atomizer.

19. An apparatus as claimed in claim 13, wherein said means for atomizing is comprised of a jet atomizer.

15 20. A method of making silica soot, said method comprising:

providing a conversion site, said conversion site for converting a silica producing feedstock into silica;

20 positioning an airblast atomizer proximate said conversion site;

delivering a silica producing feedstock in liquid form to said airblast atomizer;

25 airblast atomizing said silica producing feedstock with a gas.

30 21. A method of making silica soot, said method comprising:

providing a conversion site, said conversion site for converting a silica producing feedstock into silica;

-25-

positioning an electrostatic atomizer proximate said conversion site;

5 delivering a silica producing feedstock in liquid form to said electrostatic atomizer;

electrostatically atomizing said silica producing feedstock with an electrical charge.

10 22. A method of making silica soot, said method comprising:

providing a conversion site, said conversion site for converting a silica producing feedstock into silica;

15 positioning a pneumatic atomizer proximate said conversion site;

20 delivering a silica producing feedstock in liquid form to said pneumatic atomizer;

pneumatically atomizing said silica producing feedstock.

25 23. A method of making silica soot, said method comprising:

providing a conversion site, said conversion site for converting a silica producing feedstock into silica;

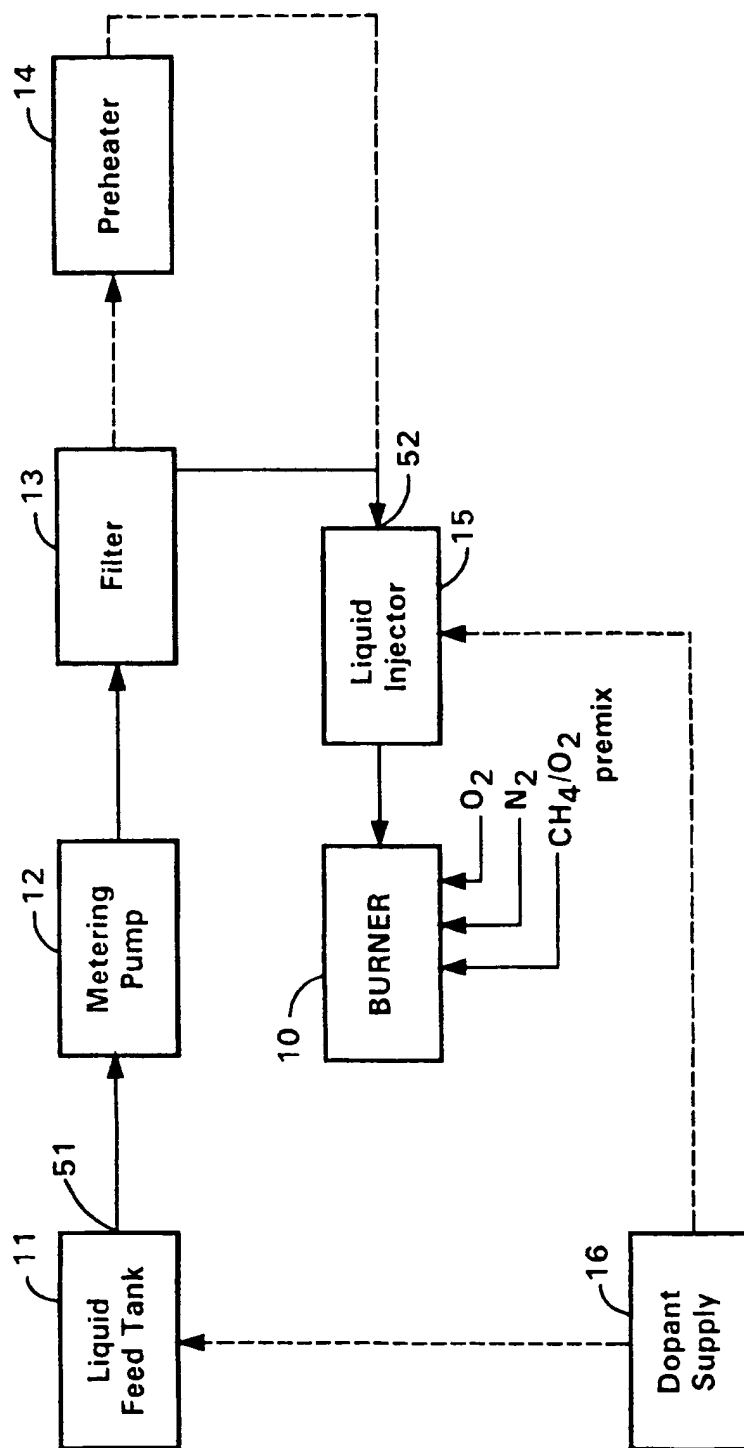
30 positioning a jet atomizer proximate said conversion site;

delivering a silica producing feedstock in liquid form to said jet atomizer;

35 jet atomizing said silica producing feedstock.

1 / 4

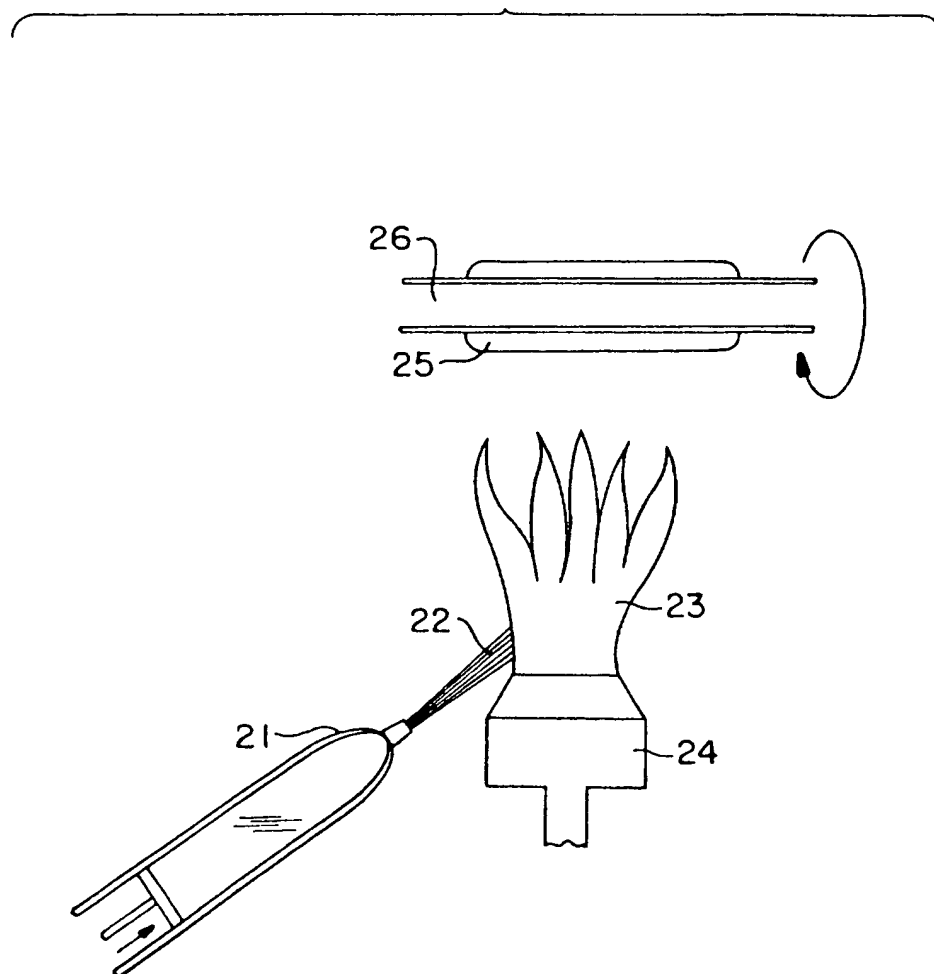
FIG. 1



SUBSTITUTE SHEET (RULE 26)

2 / 4

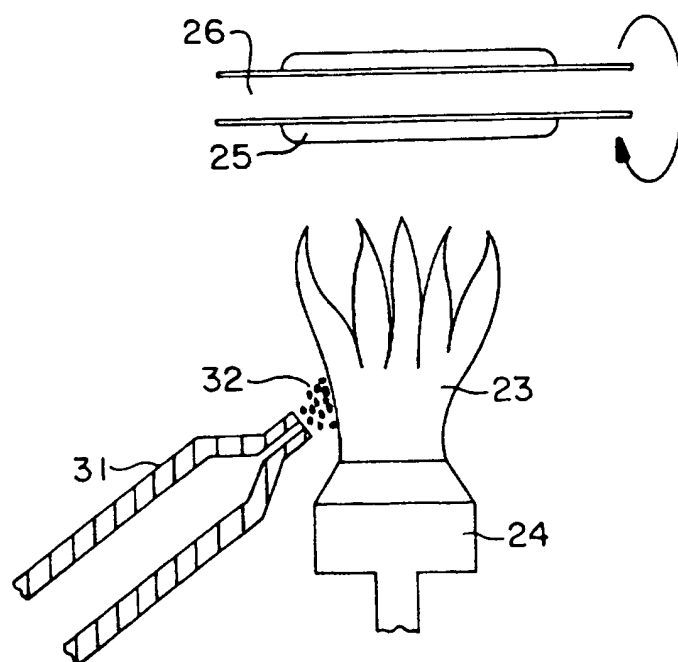
FIG. 2



SUBSTITUTE SHEET (RULE 26)

3 / 4

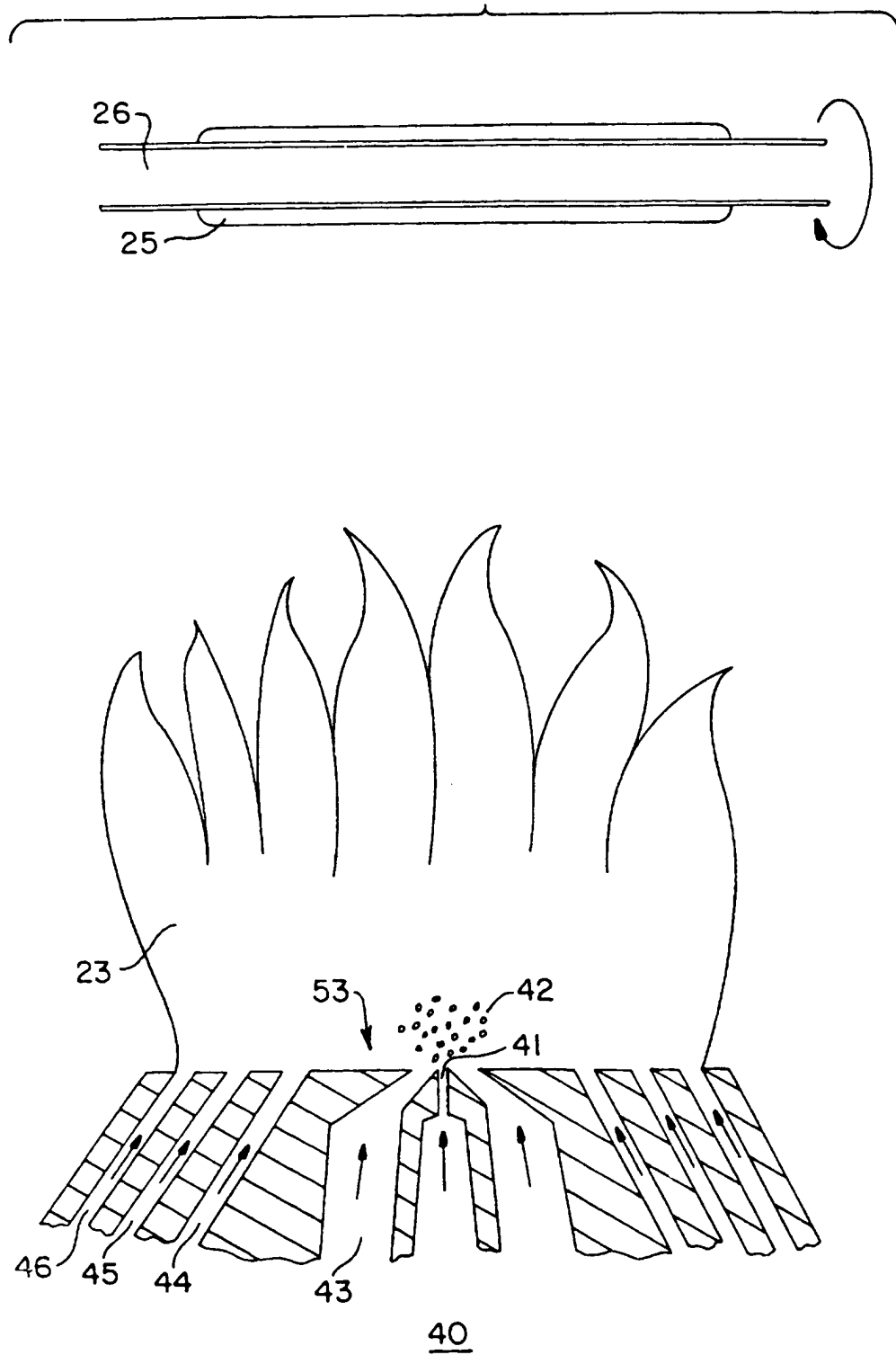
FIG. 3



SUBSTITUTE SHEET (RULE 26)

4 / 4

FIG. 4



SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/20756

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C01B 33/12; B05B 1/28

US CL : 423/337; 239/290; 422/158

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/337; 239/290; 422/158

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
423/335

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,152,819 A (BLACKWELL et al.) 06 October 1992, col. 7 lines 35-55, col. 5 lines 8-12 and Fig. 1	1, 6-12, 16
Y	US 5,297,738 A (LEHR et al.) 29 March 1994, col. 1 lines 45-55	13, 17, 21
Y	US 5,458,681 A (HASEGAWA et al.) 17 October 1995, col. 1 lines 50-60	13, 19, 23
Y	US 4,436,765 A (FENG et al.) 13 March 1984, col. 4 lines 7-16	13, 17, 18, 21, 22
Y	US 5,170,727 A (NIELSEN) 15 December 1992, col. 1 lines 33-51	2-5, 13-15, 20

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	* T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
* A* document defining the general state of the art which is not considered to be of particular relevance	* X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
* E* earlier document published on or after the international filing date	* Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
* L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	* Z* document member of the same patent family
* O* document referring to an oral disclosure, use, exhibition or other means	
* P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

06 MARCH 1997

Date of mailing of the international search report

23 APR 1997

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

STUART HENDRICKSON

Telephone No. (703) 308-2539